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Cincinnati, Ohio

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INTRODUCTION

In selecting a germicide for water treatment, certain criteria are important. The effect of pH, various ions, organic matter, temperature, and other chemical and physical factors on the microbicidal efficiency of the active agent are major considerations. Compatibility with chemicals necessary to other phases of treatment of the water supply should also be weighed. Are convenient and accurate methods available for determining the concentration of germicide applied? Is the concentration shown by the test indicative of the germicidal efficiency? Are the life span and effectiveness of the residual predictable? If laboratory data are submitted in support of the use of a germicidal agent, they should be evaluated or interpreted by someone familiar with the problems of testing such materials for use in water. Finally, having satisfied the technical criteria, is the cost in terms of equipment, space, and material acceptable?

Most of this discussion will be devoted to silver, quaternary ammonium compounds and iodine, with brief coverage of chlorine dioxide, bromine and ultraviolet light.

SECTION I: ULTRAVIOLET LIGHT (U.V.)

The use of this disinfectant is limited to special situations where other methods are not considered feasible. Because nothing is added to the water there is a minimum possibility of taste and odor problems, but no protective residual germicide is provided.

Personnel working where U.V. is used must be protected from prolonged exposure to its emanations because severe "sunburn" can occur. Protection of the eyes is particularly important. The American Medical Association has suggested tolerance limits for exposure to U.V.

The germicidal effect of U.V. is mostly limited to the output of wavelengths in the vicinity of 2570 Angstrom units. It is a good germicidal agent, but its successful use depends on adequate engineering to assure that sufficient U.V. energy actually reaches the desired point of application. The germicidal efficiency of the tubes decreases with use because the glass gradually loses its transmission efficiency. The light output should be determined at regular intervals with U.V. meters designed for the proper wavelength. The cold cathode tubes have better life expectancy and are less prone to blacken at low temperatures. Tubes should be cleaned frequently.

U.V. light will not penetrate most materials and has only limited ability to penetrate clear water. The water to be treated must be free of turbidity and color. Ordinary glass should not be interposed between the water and light source because it filters out most of the rays of germicidal wavelengths. If immersion type tubes are used, particular care must be taken to remove any deposits that form on the glass.

The cost of using U.V. is difficult to relate to the price of chlorine, but it appears that the cost of current alone would be many times that of sufficient chlorine to do the same job.

SECTION II: CHLORINE DIOXIDE

Chlorine dioxide (ClO_2) is one of the newer halogen disinfectants that have shown promise for use in water treatment. It is a powerful oxidizing agent and has a pronounced capacity to eliminate certain types of tastes and odors (1). In many similar situations, especially where phenols are present, chlorine, while an excellent germicide, frequently aggravates the taste and odor problem.

Chlorine dioxide is unstable, extremely corrosive, and a definite explosion hazard has to be considered. Exposure to light, elevation of storage temperature, or contact with organic matter can result in a violent explosion. Sodium chlorite ($NaClO_2$), from which the gas is usually generated, is also explosive. The explosiveness is readily controlled by dilution with inert gases.

Chlorine dioxide is an excellent germicide (1,2), but it has not been possible to establish valid germicidal criteria for its use because of the lack of an adequate method for accurately determining low residual concentrations of the active agent. Because it is such a strong oxidizing agent, more ClO_2 than chlorine may be required to purify polluted waters.

Factors other than the cost of the chemicals used may govern the expense of water treatment. Here, however, only cost of materials is considered. The cost of $NaClO_2$ and Cl_2 required to produce one pound of ClO_2 is about 13 times as great as that of one pound of Cl_2.

SECTION III: BROMINE

An outsider feels presumptuous in coming to Illinois to discuss the use of bromine. The work done by the Illinois Department of Health relating

to bromination of swimming pools is well known (3). Only a review of a few basic factors will be attempted here.

Bromine is a liquid at atmospheric pressure and is safer to handle than chlorine. It produces fumes which are very irritating and the liquid causes severe burns. It is a good germicidal agent and effective tests are available for determining residual concentrations. As with chlorine, the amine form is produced when ammonia is present, and the breakpoint phenomenon has been demonstrated. Bromine and monobromamine are considered nearly equal in bactericidal properties and essentially equal to free chlorine at comparable pH (4). Some of the advantages given for using bromine in swimming pools are: 1) it is easier to feed and not as hazardous to store as chlorine; 2) the bactericidal efficiency of bromamines, formed under pool conditions, is much greater than that of chloramines; 3) apparent freedom from complaints of eye irritation; and 4) odors are not troublesome. Liquid bromine costs approximately 3.5 times as much as chlorine.

SECTION IV: QUATERNARY AMMONIUM COMPOUNDS

Physical and Chemical Characteristics

Quaternary ammonium compounds (Q.A.C.) have been known since 1916. These preparations are surface active cationic compounds which ionize in water; the long chain part of the molecule carries the positive charge.

Q.A.C. are obtainable as liquids or solids. They lower the surface tension of water, and tend to foam profusely unless highly diluted. They are stable at ordinary temperatures, and in use concentrations are not usually irritating in contact with skin or mucous surfaces. In general, they are not considered corrosive in such concentrations. They are frequently marketed as strong stock solutions and in these concentrations glass

or other resistant containers such as stainless steel or monel metal are considered necessary. Because of objectionable flavors, and possible toxic effects, they have not been seriously considered for use in drinking water. The Food and Drug Administration does not permit their use in milk and food products. The present U.S. Public Health Service attitude indicates that it is unlikely that they would be acceptable in drinking water (5). They have been suggested for use to control algae in swimming pools. Another use for which they have been advocated is prevention of growths in cooling system water. Because of these water-related applications, interest in the bactericidal activity of Q.A.C. for these and similar uses is increasing.

Tests for Residual Q.A.C.

Treatment with Q.A.C. differs from halogens, such as chlorine, bromine or iodine. With the halogens the elemental form, the hydrolysis products of its reaction with water, or the N-halogen compound formed therein, is usually the active germicidal principle to be considered. The quantitative determination of the germicide present is related to the measurement of one or more of these forms. For example, chlorine might be determined as hypochlorous acid and/or chloramine. In any event, the measurement would be essentially a titration of the amount of chlorine present. With chlorine, the amount of the various forms found can be directly interpreted in terms of germicidal efficiency. In the case of Q.A.C., there is no such common denominator because each Q.A.C. is a distinct chemical entity with specific germicidal properties and therefore different from the rest. Some are much more efficient than others, and the degree to which they are affected by different waters varies widely.

The lack of an adequate test for residual Q.A.C. has been a problem. When a Q.A.C. was added to buffered distilled water and to tap water in parallel bactericidal tests, a much higher concentration of germicide was required to produce a specified percent kill in the tap water. Chemical tests for residual Q.A.C. reflected the amounts originally added to the water but did not necessarily bear a direct relation to the germicidal effect (6).

It has been stated that there is no known chemical test that will measure correlation between the bactericidal efficiency and residual of Q.A.C. in different waters (7). Tests are available for some indication of the presence or absence of uncombined Q.A.C. at levels of 150 to 200 ppm. With regard to one widely used compound, a recent communication indicated (8) that until a titration or other procedure to determine a wide range of Q.A.C. in a field test can be devised, such methods should be considered for a yes or no determination. Of another compound it has been reported that the presence of a 2.0 ppm residual can be determined, but whether this was uninhibited germicidal Q.A.C. or total active agent added is not indicated. Milk sanitation guidelines providing for the application of Q.A.C. in the absence of a satisfactory residual test are stated in the suggested Milk Ordinance and Code (9). The conditions require concentrations of sequestering agents which would not appear desirable or economically feasible where large volumes of water are to be treated. The problems related to a test for residual Q.A.C. increase enormously in application of 1 to 5 ppm concentrations, suggested for control of algae in swimming pools. Research on development of a satisfactory test for residual Q.A.C. is continuing.

Before use by anyone charged with the responsibility of protecting the health of the public through the use of Q.A.C., any such test should be evaluated by parallel germicidal tests, with concentrations of the Q.A.C. considered for use in practice, in buffered distilled water and in a variety of different waters in which it will be used. The bactericidal test suggested in the Milk Ordinance and Code (10) has been extensively used for testing germicides for water treatment. The chemical test should measure concentrations of Q.A.C. related to the bactericidal effect and not merely reflect the amount of germicide originally added. An example would be a chlorine test in which the bactericidal effect is directly related to the post-breakpoint residual but not to the total chlorine originally applied.

Effect of Environmental Conditions

The bactericidal efficiency of Q.A.C. is markedly affected by environment. It increases with temperature. The germicidal efficiency of most Q.A.C. currently on the market increases with pH in the range 7.0 to 8.5 or 9.0. However, there are exceptions to this statement (6), and new products are continually being developed. There is currently on the market one compound with efficiency reported to be unaffected by wide variations in pH.

The efficiency of Q.A.C. can be affected to an enormous degree by the nature of additives used in preparing a formulation. In a series of tests, equal concentrations of a given Q.A.C. as pure active agent and as a combined detergent sanitizer were examined under parallel conditions. Results obtained in these tests are presented in Table 1. In one water the germicidal effect

of the Q.A.C. was almost eliminated by the inclusion of the detergent; the efficiency of the cationic germicide had largely been nullified by compounding with an anionic detergent. Soaps also interfere, and in swimming pool use it may be necessary to consider these factors.

Effect of Different Waters

In an early investigation of Q.A.C., interference of different tap waters with the germicidal action of these compounds was noted (11). It was determined that the interference reaction observed took place rather rapidly and did not progress to any appreciable degree in tests extending over a 24-hour period.

In a later study (12) the effect of hardness and other mineral components was extensively investigated. Severe interference with bactericidal action was observed in hard water. In these waters the calcium and magnesium were mostly present as bicarbonate. Boiling for two hours resulted in a significant reduction in interference. This could be due either to precipitation of calcium and/or magnesium as carbonates or to destruction of bicarbonates. Q.A.C. were tested in distilled water containing 375 ppm of calcium bicarbonate ($Ca(HCO_3)_2$), 375 ppm of magnesium bicarbonate ($Mg(HCO_3)_2$), and also with an equivalent amount of bicarbonate as the sodium salt. The data obtained in these tests indicate that bicarbonate did not cause the interference.

Is there a difference in the effect of permanent hardness and temporary (bicarbonate) hardness? These factors were evaluated in the laboratory by preparing synthetic waters containing 375 ppm of hardness as $MgSO_4$, $MgCl_2$, $CaSO_4$, $CaCl_2$, respectively. The results indicate that a unit of hardness is

essentially a unit of interference regardless of the nature of the hardness (Table 2), as was later confirmed in field studies with natural waters containing permanent hardness. The effect of naturally occurring alkaline waters was also examined. In such a water having a total hardness of 8 ppm and mineral content of 252 ppm, the germicidal efficiency of Q.A.C. approached that noted in tests with distilled water and $NaHCO_3$ water.

Effect of Softening

The effect on Q.A.C. of various methods of softening a hard water were evaluated in the laboratory. In these studies an initial temporary hardness of 415 ppm was reduced to 70 to 75 ppm. The desired level of hardness in zeolite treated water was obtained by admixture with the required amount of untreated water. The addition of amounts of sequestering agents which reduced hardness to a similar level generally resulted in an approximately equivalent reduction in interference. However, there was one important exception with no evidence of any reduction in interference. This occurred with sodium hexametaphosphate, a compound frequently used in water treatment. In further tests the substitution of tetrasodium pyrophosphate yielded a satisfactory result. With most compounds the best sequestering agent was the tetrasodium salt of ethylene-diamine-tetra-acetic acid. No single sequestering agent was equally effective with all compounds. These findings are further evidence that each Q.A.C. should be considered as an individual entity.

There has been some question regarding the effect of iron on Q.A.C. The work previously reported in the literature deals only with ferric iron (Fe^{+++}). In highly carbonated waters iron is usually present as ferrous

bicarbonate ($Fe(HCO_3)_2$) which is rather rapidly oxidized to the ferric form. In treating freshly drawn well water for emergency sterilization of equipment, or such a water in closed systems, the effect of the bicarbonate form could be important. Ferrous bicarbonate was produced in a closed system and used in bactericidal tests in flasks overlaid with an atmosphere of oxygen-free nitrogen. Chemical analysis at the conclusion of the test verified the absence of ferric iron. The data indicate that the interference of ferrous iron at concentrations found in wells or most municipal supplies probably would not be significant unless a very low concentration (1-5 ppm) of a Q.A.C. is being considered.

Small amounts of strontium, barium, and silica are found in natural waters. Tests were run with 20 ppm of silica as sodium silicate and 1.0 and 2.5 ppm, respectively, of barium and strontium as bicarbonate. At the concentrations used, these compounds did not significantly affect the bactericidal efficiency of solutions containing 50 ppm of Q.A.C.

Reasonably adequate criteria to govern the use of a number of Q.A.C. at concentrations of 50 ppm or more appear to be available. For their use at low concentrations (1.0-5.0 ppm) with longer contact times, the present state of knowledge is not considered adequate. However, where a given mineral interferes, there is little probability that reducing the Q.A.C. concentration would improve the situation. Additional research, conducted under carefully controlled conditions, is needed to evaluate the effect of environmental factors on low concentrations of Q.A.C. This information is absolutely essential to establish adequate time-concentration relationships under varying conditions of pH, temperature, and water hardness. Research is hampered by

lack of a chemical test to determine the concentration of residual Q.A.C. in such manner that it can be interpreted in terms of germicidal effect.

Adsorption from Solution

If Q.A.C. are used in plant cleanup procedures, unlimited contact with mops and similar materials should be avoided. Some additional Q.A.C. should be added to allow for demand of such articles. Cotton materials, such as gauze, adsorb significant amounts of Q.A.C., reducing the effective concentration of the germicide in solution. This has been demonstrated in a number of unfortunate episodes resulting in the transmission of serious infections. In one outbreak 40 cases were traced to gauze pads stored in a Q.A.C. solution.

Sampling Precautions

If low concentrations of Q.A.C. are used with chlorine to control algae in swimming pools, extra care is needed in taking water samples for bacteriological analysis. It is desirable to maintain in a viable state until the sample is inoculated in the laboratory, all organisms alive at the time the sample was collected. The sodium thiosulfate ($Na_2S_2O_3$) usually included in sample bottles would neutralize the chlorine. It would not effectively neutralize the Q.A.C. Therefore, a good neutralizer for Q.A.C. should also be included (13). If the time in transport between sampling and inoculation is considerable, it is possible that, in the absence of a neutralizer, the Q.A.C. in the sample could exert a bacteriostatic or bactericidal effect on organisms alive and viable at the time the sample was taken. Judging the quality of the water on the basis of such data could be misleading.

It is impossible to give a cost figure for treating water with all of the Q.A.C. available. The price of one widely distributed Q.A.C., alkyl dimethyl benzyl ammonium chloride, is $3.75 per gallon of a solution containing 10 percent of active agent, or $4.52 per pound of active agent. Therefore, the cost of treating water with 1.0 ppm of this compound, all other factors being equal, would be approximately 72 times the cost of treatment with 1.0 ppm of chlorine.

SECTION V: SILVER

General Considerations

Silver has a particular affinity for sulfur and halogen elements. Everyone is familiar with the ease with which silver tarnishes. This is an example of the reaction of silver with sulfur, resulting in the production of silver sulfide (Ag_2S). These reactions are utilized in numerous analytical methods.

Crystalline silver nitrate ($AgNO_3$), a form frequently used in chemical work, is extremely caustic to body fluids, moist skin, or mucous surfaces. So are strong aqueous solutions of $AgNO_3$, and care must be exercised in handling them.

Silver is readily ionized by electrolysis, and this property is the basis for some of the systems used in the germicidal treatment of water. Silver concentrations usually considered for water treatment are in the range of 25 to 75 ppb.

Water Treatment Considerations

One of the advantages of using silver for water treatment is that it does not itself produce color, taste, or odor, nor, so far as is known, form addition products that do so. The residual may persist for a considerable period of time, often many days. The bactericidal effect of silver appears to be less susceptible than that of free chlorine to interference by organic mater. Space requirements for equipment and storage of material are moderate.

Measurement of Silver

In order to control effectively the conditions under which a very low concentration of silver is used in practical applications or germicidal

tests, an accurate method is necessary for determining the amount of silver present. A variety of tests have been evaluated (14). The silver concentrations used in water treatment are so small that a very sensitive test is needed. A modification (14) of the rhodanine test (15) and a spot test (16,17) appear to be the best. The modified rhodanine test was used in the laboratory in distilled water. A new set of standards should be prepared each time the test is run. The test is delicate and anyone using it must be thoroughly familiar with its idiosyncracies. It is subject to a variety of interferences in tap waters of varying mineral content. A recent adaptation of this test offers promise of overcoming the interference in tap waters (18).

The spot test has frequently been suggested and would be a convenient and practical field test if some of the problems related to its use could be resolved. In this test, the silver is precipitated as silver iodide (AgI). The sample is then filtered through a membrane filter*. The pale yellow AgI is converted to Ag_2S, which is black. The results are interpreted by comparing the unknown spot with a series of standards prepared by filtering solutions to which known amounts of $AgNO_3$ have been added. Unfortunately, a variety of factors affect this test.

All of the silver present in either the sample, or standards prepared under parallel conditions, is not retained on the filter. When the sample is shaken for five minutes before filtering, significantly more silver is recovered, and this is further increased when a finer filter is used. However, in tests with Ag^{110m} it was demonstrated that even with

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*H.A. "Millipore" type, manufactured by The Millipore Company is for identification only and does not signify endorsement by the Public Health Service.

the combination of shaking and the finer filter, approximately 15 percent of the silver remained in the filtrate. Adsorption on glass in the test flasks also significantly reduced the amount of silver recovered.

It is possible that the spot test might result in reporting considerably less silver than actually present. Such an error might have an advantage because the excess silver would provide an added bactericidal margin. Unfortunately, the total might exceed the maximum concentration of silver permitted for use in drinking water. In the Public Health Service Drinking Water Standards, now under revision, a maximum silver concentration of 50 ppb is being considered.

Adsorption

The adsorption of silver by glass and other materials creates problems both in evaluating the bactericidal effect of silver in the laboratory and in using it for water treatment. When silver, at a concentration advocated for use in water treatment is used in tests in "Pyrex"* flasks, a significant amount is adsorbed from the test solution and this introduces an error. In the work reported, this loss was minimized but not completely eliminated, as was demonstrated by bactericidal examinations and the use of radioactive Ag^{110m}. The same amount of $AgNO_3$ was added to distilled water in a series of flasks and allowed to stand at room temperature for eighteen and one-half hours and in a similar set for one hour before E. coli suspension was added to all flasks. The data obtained in these tests are presented in Table 3. A significant reduction in the bactericidal effect is noted. E. coli was also used in all

*Tradename used for identification only.

subsequent tests with silver. The use of distilled water eliminated the possibility that any silver lost was inactivated by minerals in the water.

Silver adsorbed by glass is not adequately removed by the usual cleaning methods. "Pyrex" tubes contaminated with a solution containing 1.0 ppm of Ag^{110m} were cleaned with strong dichromate cleaning solution. Distilled water was then allowed to stand in these tubes for 18-1/2 hours, after which bacteria were added. A marked reduction in bacterial survival was caused by silver desorbed from the glass, and this desorption was further confirmed by the Ag^{110m} tests (Table 4).

The growth-inhibiting effect of adsorbed silver released by glass is important to anyone considering its use for water treatment. Silver retained on a glass sample bottle can be released to a subsequent sample even if the container has been sterilized before reuse. The potential for error is evident, and added precautions are necessary. The residual silver can be removed by boiling glassware in strong sodium chloride (NaCl) solution.

Neutralizers

Neutralizers are important from the standpoint of sampling as well as in laboratory testing, because silver is frequently bacteriostatic at low concentrations. This means that the organisms are dormant, not growing but not killed. It is therefore desirable to include a good neutralizer in bottles used for collecting silver bearing waters. A mixture of sodium thioglycollate and sodium thiosulfate will take care of both silver and chlorine. Sodium thiosulfate appears to be less effective with silver than sodium thioglycollate.

Different Sources of Silver

The effect of the source or origin of silver on its germicidal efficiency has been subject to much discussion. Does a given concentration of silver, 50 ppb for example, from $AgNO_3$, exert the same bactericidal effect as an equivalent amount obtained from a filter device? Is colloidal silver especially germicidal or is the colloid merely a means of expanding surface area so ions can more easily get into solution? By careful equilibration of glassware, parallel tests, and much replication, the effect of variations has been minimized to a point where mean values provide the basis for valid conclusions.

A highly concentrated opaque colloidal silver preparation was centrifuged at 100,000 g for 3-1/2 hours to remove colloidal matter. Equal volumes of supernatant and uncentrifuged material were then used in parallel bactericidal tests. Although the test water receiving the uncentrifuged formulations contained many times as much silver as that receiving the supernatant, the two were almost identical in germicidal efficiency. The results suggest that both the uncentrifuged stock preparation and the supernatant contained silver ions at equilibrium concentrations, the particulate silver in the stock preparation serving only as a source of supply. While these solutions could not be analyzed, the kill obtained with 40 ppb of silver as $AgNO_3$ under similar conditions was essentially the same. These data are presented in Figure 1.

Parallel tests were also made with 40 ppb concentrations of silver as effluent from a filter device and as $AgNO_3$. It is well known that silver is a less efficient germicide at low pH (6.1) than at higher pH (7.5). However, it <u>is</u> germicidal at pH 6.1, given sufficient time. Low silver content was employed to extend kill curves which would provide a good

basis for comparing the effect of silver from the two sources. Distilled water was used to eliminate interference of minerals with either the chemical analyses or the bactericidal action of the silver. The low pH was selected because this was the pH at which the distilled water stabilized in the tests. The results obtained in these examinations are presented in Table 5. The similarity of the kill obtained with silver from the two sources, one of which was unquestionably ionic ($AgNO_3$), indicates that the silver ion is the germicidal principle.

Environmental Factors

Increasing pH significantly improves the bactericidal efficiency of silver. Phosphate interferes with the action of silver to a moderate degree. In tests at pH 7.5 in $\frac{M}{1500}$ phosphate buffer a 99.0 percent kill of E. coli was obtained in three hours with 40 ppb of silver as $AgNO_3$. The germicidal efficiency of silver is seriously reduced by low temperatures, and it should not be used at temperatures below 5° C. At temperatures up to 10° C, long holding times would be necessary. The efficiency of silver is affected by minerals or other constituents found in well and tap waters. In tests with the same amount of silver in synthetic phosphate water, Cincinnati tap water, and water from Norwood, Ohio, municipal wells, which contained about 400 ppm of hardness, the kill time increased with increasing mineral content. In laboratory tests using E. coli grown on agar media, increasing the organism load from 1,800 to 1,800,000 cells per ml did not perceptibly affect the efficiency of silver as $AgNO_3$ in concentrations from 10 to 35 ppb.

In the work reported, it was not possible to investigate the effect of a variety of ions found in natural waters. The findings in much of the earlier work are of questionable value because of inadequate control of

test conditions. Recent work (19), in which a rather high degree of control has been exercised, indicates that calcium, phosphate, and chloride ions interfere with the action of silver. It was pointed out that Ag^+ and Cl^- combinations still retained some germicidal activity. Other workers (17) have reported on the effect of mineral content and have suggested 1.0 ppm of sulfide as the maximum permissible.

Practical Application

Silver can be applied as a liquid, by desorption from filter beds of silver coated sand, carbon, fabric, or other materials, and by electrolytic decomposition of metallic silver. Preparations, such as $AgNO_3$ or colloidal suspensions, with automatic dosing systems, could be used to maintain the desired feed rates. Such methods might be considered in larger installations where supervision is available, but they would be subject to many of the same problems which have limited the use of other liquid germicides in homes and various small systems.

Silver sands and other filter devices have been advocated as self-limiting dosage methods because the maximum amount of silver that could be added would probably range, in most instances, from 30 to 300 ppb. An advantage might be the ease with which some of these methods of applying silver could be fitted into a conventional water treatment operation. The filter would presumably have some value, depending on the porosity, depth of bed, and other factors, for removing Endamoeba histolytica cysts which silver does not kill at practical concentrations (20).

In some of the silver-releasing filter systems there is a rapid "knockdown" in the filter. The organisms surviving in the filtrate are killed at a rate determined by the residual silver in the water. The

practice with such systems is to tailor the transit time in the filter to a maximum flow rate which, considering the minimum post-filtration retention time, will reduce the coliform count of treated water to an acceptable level. Such units are designed to handle a specified maximum pollutional load. When this is exceeded an unsafe water results. Therefore, the design of a given installation should be adequate to handle the maximum level of pollution that can occur in the source water. The bactericidal efficiency is determined by the combined effect of filtration and residual. This complicates the control of such a unit because it is difficult to relate the concentration of silver in the effluent to the germicidal effect. This is particularly true when the source water is subject to unexpected surges in pollution.

Household units are designed to yield water having a predetermined silver concentration when operated at a specified rate of flow. Fluctuations in flow can result in wide variations in the amount of silver delivered at the tap.

What, for example, is the effect of slow leaks found in so many home systems? Filter units, operated at reduced flow rates, deliver water containing a much higher silver concentration. Someone periodically drawing a glass of water would consume much more silver than if the unit operated at the capacity for which it was designed. The effect of increased silver content of the water is further emphasized when such water is used in cooking. The silver-concentrating effect of extracting silver from water used to cook cabbage and other vegetables containing sulfur could also result in a marked increase in the amount of silver ingested.

The rate at which silver is added by electrolytic decomposition of metallic silver is directly related to the amount of current applied. Dosage can be increased or decreased by varying the current flow, and power consumption is low.

Because of the slow bactericidal action of silver at the concentrations considered, its value as a protective residual is limited. This is especially evident in swimming pools where a rapid kill of freshly added infectious material is desirable.

Silver bullion costs 233 times as much as chlorine. The processed forms are considerably more expensive. Therefore, after making reasonable allowance for the use of a lower concentration of silver than of other disinfectants, it appears that the application of silver is limited to situations where cost is not a primary consideration.

SECTION VI: IODINE

Physical and Chemical Characteristics

The iodine of commerce is a nonmetallic solid. It is usually referred to as "metallic" iodine and has the appearance of dark, shiny, thin pieces of metal. In this form it is corrosive and ordinary metal containers are unsuitable for shipping or storing it. It is dense and sublimates slowly at room temperatures. When heated, it forms a beautiful violet vapor. The hazards due to toxic vapors of iodine are less than with the other halogens used in germicidal treatment of water. The vapor pressure of iodine at 25° C is only 0.31 mm. The corresponding figures for bromine and chlorine are 215 and 5,300 mm, respectively.

At room temperature, the solubility of iodine in ethyl alcohol is 27.0 percent, but only 0.03 percent in water. The solubility in water can

be markedly increased by adding iodide. Contact of metallic iodine with ammonia gas or solutions is hazardous because nitrogen triiodide (NI_3) and the related ammoniacal compound ($NI_3 \cdot NH_3$) are formed. These combinations are detonated by very minor shocks.

In aqueous solution, titrable iodine exists in several forms. Hypoiodous acid (HOI) and molecular iodine (I_2) are the germicidal forms of importance. When iodide (I^-) is added to give an I_2 to I^- molar ratio of 1:1.2, titrable iodine also exists as triiodide ion (I_3^-). The concentration of each form of tritrable iodine in the solution depends on the pH, total titrable iodine, and I_2 - I^- molar ratio.

At or below pH 6.0 and 7.0, with a total titrable iodine concentration of more than 0.5 and 5.0 ppm respectively, all of the titrable iodine is I_2. When pH is increased to 8.0, computations show that the amount of I_2 hydrolyzed ranges from approximately 20 to 90 percent at titrable iodine concentrations of 20 to 30 ppm and 0.5 ppm, respectively (21).

This calculation is affected to a degree by the decomposition of HOI to iodate (IO^-), which is non-germicidal (22). The destruction of HOI becomes significant at pH 8.0 and increases with increasing pH. It has been suggested that up to pH 8.0 differences in the ratio of I_2 to HOI can be ignored and that, under most of the more difficult operating conditions, the application of a 10 to 15 percent excess of total titrable iodine should be adequate to eliminate the need for determining the ratio of the various germicidal forms present (21). Therefore, these factors would not be a problem in plant treatment of water, because iodide presumably would not be used as a solubilizing agent and is not normally present in

water. The hydrolysis of I_2 and decomposition of HOI are represented by the following equations:

(1) $I_2 + H_2O \longrightarrow HOI + H^+ + I^-$

(2) $3HOI + 2(OH)^- \rightleftharpoons HIO_3 + 2H_2O + 2I^-$

When I^- ion is present, as is the case with common elemental iodine preparations such as tincture of iodine and iodine tablets which contain I_2 and I^- in a molar ratio of 1:1, significant amounts of triiodide ion (I_3^-) are formed only at concentrations over 20 ppm. For practical purposes, at this ratio, if the pH is below 7.0 and the titrable iodine concentration does not exceed 20.0 ppm, essentially all of the iodine is present as I_2. At higher pH this problem is minimized because less I_3^- is formed. Triiodide ion is only weakly germicidal (21). For purposes of this discussion, iodine concentrations as high as 20.0 ppm are not considered and I_3^- is not a problem.

Iodine is not considered to form iodamines under conditions prevailing in treatable waters. Colored waters interfere with the action of iodine (23).

The effect of various buffer ions in hastening decomposition of HOI at pH values above 8.0 is also a problem. Phosphates are particularly bad in this respect (22,24), while borate, citrate, and carbonate do not cause serious interference. This problem results from the fact that some buffers accelerate the formation of IO^-, the effect being that of a catalyst.

Plant treatment of large volumes of water with iodine would not ordinarily be economically feasible because it is significantly more expensive than chlorine, in terms of cost per unit of germicidal effectiveness. In addition, before iodine can be considered for universal

water disinfection, its levels for human ingestion without physiological complications must be more fully understood. Accordingly, insofar as drinking water is concerned, emergency use is all that should presently be considered.

What then are some of the factors that might justify the use of iodine for treatment of water? Iodine is considered to have advantages for use in swimming pools because it avoids the eye irritations sometimes encountered with chlorine (25). It has been reported to be less affected by fluctuation in bathing loads and to be relatively free of taste and odor problems (26). Combined treatment with iodine and chlorine has been reported to have advantages in swimming pools but the degree of control necessary to success with this method has limited its use. Because of its storage stability, it could be considered for emergency use in catastrophe situations. Under these conditions, admitting some disadvantages, its use could be adapted to plant treatment of water in the event of a chlorine shortage. It could also be used in the emergency disinfection of small volumes of water such as canteens as well as for field units and private supplies.

Iodine Releasing Preparations

Iodine has been prepared in a variety of solid forms for emergency treatment of small volumes of water. These preparations release free iodine when dissolved in water.

The deterioration of an iodine-releasing preparation is illustrated by data obtained in studies of the effect of storage at 120° F. These data are presented in Table 6. The tablets used in these tests were hermetically sealed in foil envelopes (27). The following comments are not intended as an indictment of such preparations. Rather, they are

presented as an example of the need for frequent determination of potency when there is no alternative to storage under adverse conditions. It has been shown that storage stability at 130° F, in wax sealed bottles, was good for intervals up to eight weeks but losses of 10 to 20 percent were noted after 24 weeks (28). Frequent opening and/or open storage under hot humid conditions results in rapid deterioration of such formulations. The temperatures mentioned are not excessive because they are readily attained in emergency situations with storage under canvas or in unshaded temporary buildings.

Dosage Criteria

The effect of iodine on viruses has been considered because they are among the more resistant pathogenic forms encountered. The viricidal activity has been investigated with a number of enteroviruses. In these studies the virus suspensions were shown to be free of demonstrable demand effects (29). The data obtained in this work are presented in Figure 2.

It is immediately apparent, when compared with bactericidal data presented later, that the viruses are much more resistant than the vegetative bacteria. The behavior of the poliovirus I (Lotshaw strain) is particularly interesting. This virus was isolated from a patient paralyzed with poliomyelitis and presumably was highly neurotrophic since it was used with no further passage after isolation. The Mahoney strain had previously been fed to human volunteers without ill effect.

The Army considers 20-minute exposure to 8.0 ppm of iodine to be adequate (30). Other workers suggest that 10-minute exposure to 8.0 ppm is adequate for most waters with the time extended to 20 minutes if the water is cold; doubling the concentration was effective with all waters containing such resistant organisms as E. histolytica (28).

Potability of water treated with 8.0 ppm of iodine was higher than for that treated with acceptable concentrations of chlorine (27). The substitution of alcoholic tincture of iodine for iodine-releasing preparations results in decreased potability.

One of the factors in establishing the 8.0 ppm concentration was that toxic effects are more of a problem in hot climates. The hypersensitive response of some individuals to iodine may be considered, although the exigencies of the emergency usually outweigh these considerations because of the limited number of persons who would be affected. In tablet preparations, iodides are frequently used to increase the solubility of iodine. This further increases the amount of iodine ingested. However, research relating to the possible undesirable physiological effect of ingesting iodine over long periods is continuing.

With the short time exposures usually prevailing under such conditions, the high concentrations of iodine indicated are necessary to kill E. histolytica. In plant treatment or large field units these factors are not serious because filtration is presumed to remove cysts and ova. Taste and odor problems resulting from the high concentrations of iodine needed with short contact times can generally be reduced by using a neutralizer. However, the problems of adequate application of such a method, by diverse segments of a population, present difficulties that offset most of the advantages. For example, reversal of the order of adding the neutralizer and iodine-releasing tablets would result in no germicidal treatment.

Use of Low Iodine Concentrations

The bactericidal action of iodine was evaluated in an extensive investigation of low concentrations of an order which might be used in emergency disinfection of large volumes of water where longer holding times would be possible (31). Iodine has certain properties that make it difficult to work with at low concentrations. For example, in establishing the minimum concentration of post-breakpoint chlorine which would kill with a one- to two-hour exposure, chlorine concentrations of 0.02 - 0.05 ppm were added initially and successfully maintained throughout a bactericidal test (32). With iodine, concentrations giving comparable survival times were too low to be accurately measured by chemical methods. This problem was solved by developing a satisfactory method in which an amperometer was used (22). It had the added advantage that iodine was titrated at the pH of the test solution.

The amperometric determination of iodine has been found to be accurate within ± 0.01 ppm in concentration ranges of 0.2 to 2.0 ppm. Because this method measures primarily HOI and molecular I_2, and these are considered the forms which are germicidal, the amperometric analysis bears a direct relationship to the germicidal efficiency. Because some of the iodine is decomposed to IO^-, it was not possible to maintain the extremely low iodine concentration necessary to a critical demand test. Iodine is chemically less active than chlorine. Therefore, water free of chlorine demand should be at least equally free of iodine demand. Such a water, having a chlorine demand of considerably less than 0.01 ppm, was used in these tests.

Because of the conversion of iodine to iodates at pH values above 8.0, even with the best buffers, some depletion of germicidal iodine occurred during

an experiment. Percentage-wise, at iodine levels below 0.2 ppm the loss was so great that the concentration could not be maintained at a satisfactorily constant value during an experiment. Consequently, extended kill curves for use in practical application of low concentrations of iodine, where long retention times are available, could not be provided. At increased iodine dosages the percentage loss was not sufficient to seriously affect the work. The following species of bacteria were used in this study and included: 1) laboratory strains of Salmonella typhosa and cultures freshly isolated from the blood of typhoid patients, 2) Salmonella paratyphi and typhi murium, 3) two strains of E. coli and one of Aerobacter aerogenes, 4) one strain of Streptococcus fecalis and, 5) one freshly isolated strain each of Shigella schottmuelleri, dysentariae II, flexneri I and sonnei I. In these tests it was determined that the bacteria added exerted no measurable iodine demand (31).

S. typhosa and Sh. sonnei were, respectively, the least and the most resistant organisms encountered. The higher resistance of Sh. sonnei was clearly evident only under a combination of the most adverse conditions of pH and temperature (pH 9.15 at 2.0 - 5.0°C). After continued growth on artificial media for six months there appeared to be a significant loss in resistance by the freshly isolated Shigellae. Results obtained with the more resistant species are presented in Figure 3. These results indicate the desirability of providing an adequate safety factor over and above the amount of iodine required to kill E. coli. It is apparent that, as with chlorine, pH and temperature are factors which have to be carefully considered. The minimum concentration which killed all species in one minute, under the

most adverse conditions, was 4.3 ppm. The minimum concentrations effective with all species after a five-minute exposure at pH 9.15 ranged from less than 0.4 ppm to 3.5 ppm at 2.0 - 5.0°C and from 0.2 to slightly less than 0.8 ppm at 20 - 26°C. The efficiency of iodine was significantly reduced at higher pH's, particularly when temperatures were low.

The use of iodine in plant treatment is not recommended and should not be considered except in an emergency where more suitable materials are not available. Under these conditions economic considerations would limit the use of iodine to low concentrations. The holding times necessary to significantly reduce virus populations could probably be attained. With the more resistant strains, such as Lotshaw I and Coxsackie A9, 1.0 ppm of iodine would probably be adequate with a three to four-hour exposure. Because of the long contact time necessary at low iodine concentrations, if the ultimate in virus reduction is considered, the desirability of applying iodine at the earliest possible point in water treatment is obvious. In present water works practice, the degree of treatment which reduces the coliform count to the specified level is generally considered adequate for water treated with chlorine. The application of the same criteria to treatment with iodine would appear reasonable.

Problems in Plant Application

The solubilization of large amounts of iodine in water would be a major problem in water works practice. Preparation of stock solutions of iodine by dissolving in alcohol or in water with an iodide to improve solubility would be economically prohibitive on such a large scale. However, these problems were successfully resolved in one instance where iodine was

the only germicide used in treating a public water supply (33). In this work it took five days, using 1.0 gram of pulverized iodine per liter of water, to produce a solution containing 220 ppm of iodine. This was a relatively strong solution because the saturation point of an aqueous iodine solution is 293 ppm at 20°C (34). Interpreted in terms of water works practice this would mean that to produce 1,000,000 gallons of water containing 1.0 ppm of iodine approximately 3,400 gallons of saturated aqueous stock solution would be needed. At decreasing temperatures the problem would become increasingly critical.

In the work previously cited, this problem was reduced in magnitude as follows: the iodine was finely ground and combined with sand to form a filter. With this system, in 24 hours, one volume of filter bed produced 1,920 volumes of effluent, containing 135 ppm of iodine. The ratio of depth to cross section area in the filter was 28:1. With this arrangement, approximately 3.85 gallons of filter bed, operated continuously, would provide 1.0 ppm of iodine for 1,000,000 gallons of water in 24 hours. This equipment was considered much more easily managed than that used in the application of chlorine and not subject to the breakdowns that often occur with chlorine equipment.

The cost of treatment with iodine is much higher than with chlorine. The price of iodine (99 percent pure) is $1.10 per pound in keg lots of approximately 143 pounds. No discount is available even on ton lots. The corresponding price of liquid chlorine was $0.0625 per pound. Therefore, it would cost approximately $9.10 to treat 1,000,000 gallons of water with 1.0 ppm of iodine. This is roughly 18 times as much as the cost of an

equivalent amount of chlorine. While some reduction in dosage with iodine might be considered because of probable increased persistence of the germicidal residual, the economics are strongly against the use of iodine as a substitute for chlorine except under circumstances where cost is a secondary consideration.

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TABLE 1. EFFECT OF DIFFERENT WATERS ON Q.A.C.

Germicide	Results obtained at room temperature								
	Buffered distilled			Cincinnati tap			Norwood tap		
	ppm required to kill all *E. coli* in minutes								
	1	2	5	1	2	5	1	2	5
Q.A.C. + detergent	30	30	5	500	400	400	15,000+	15,000+	15,000+
Q.A.C. only	10	—	2.5	100	80	50	140	120	40

TABLE 2. EFFECT OF HARDNESS ON Q.A.C.*

50 ppm Q.A.C.	pH		Percent of E. coli surviving at 22° C after (minutes)		
	Initial	Final	2	5	10
$MgSO_4$	8.1	7.3	85	22	0.076
$MgCl_2$	8.9	8.2	90	24	0.10
$Mg(HCO_3)_2$	8.3	8.3	11	0.85	0.0003
$CaSO_4$	8.2	7.5	81	49	2.3
$CaCl_2$	8.3	8.0	92	68	6.6
$Ca(HCO_3)_2$	7.4	7.4	77	48	8.9
$NaHCO_3$	7.5	7.9	0		

*All solutions are equivalent to 375 ppm $CaCO_3$ in distilled water.

TABLE 3. EFFECT OF CONTACT WITH GLASS ON GERMICIDAL EFFICIENCY OF $AgNO_3$ IN DISTILLED WATER AT pH 6.2[1]

ppb Ag[2]	Contact time[3]	Percent of bacteria surviving for:							
		15 Min.	30 Min.	1 Hr.	2 Hrs.	3 Hrs.	4 Hrs.	5 Hrs.	6 Hrs.
35	1 Hr.	38.1	37.1	29.0	16.7	8.90	3.43	0.81	0.84
35	18-½ Hrs.	86.2	71.4	60.5	36.7	27.6	16.0	11.8	5.96
70	1 Hr.	61.4	38.1	31.9	8.0	1.10	~0.01	0	0
70	18-½ Hrs.	71.4	61.9	41.9	15.0	6.57	0.26	0.07	0

(1) Representative experiment.
(2) Amount of Ag initially added.
(3) Elapsed time between adding test solution to flask and adding test suspension.

TABLE 4. GERMICIDAL EFFECT OF DESORBED Ag^{110m}

Tube No.(1)	ppm Ag^{110m}(2)	Micrograms Ag^{110m} (3) adsorbed	Percent of bacteria surviving for:		
			2 Hrs.	4 Hrs.	6 Hrs.
Control(4)	10,000	3.00	0	0	0
Av. 131 & 141	1,000	2.92	9.47	0	0
142	320	2.35	8.33	1.66	0
143	100	3.36	6.10	0.76	0
Av. 135 & 145	10	1.86	0.35	0	0
Av. 137 & 147	1	1.92	3.20	0.80	0
Av. 328 & 329	0.2	0.27	96.1	86.1	76.1
Colloidal(5)	Undiluted(6)	...	18.0	3.32	1.72

(1) Full of $Ag^{110m}NO_3$ solution during contamination period.
(2) In toxifying solution.
(3) The amount of adsorbed silver remaining after dichromate cleaning is not reported because tubes could not be counted subsequent to dichromate treatment due to danger of bacterial contamination by probe. However, tubes treated in a parallel fashion were counted and showed that dichromate cleaning removed 35-60 percent of the residual silver.
(4) Flow-through rinse only, no subsequent dichromate cleaning.
(5) Colloidal Ag^{110m} was not available.
(6) Undiluted gross material in commercial product was used - actual Ag content not known.

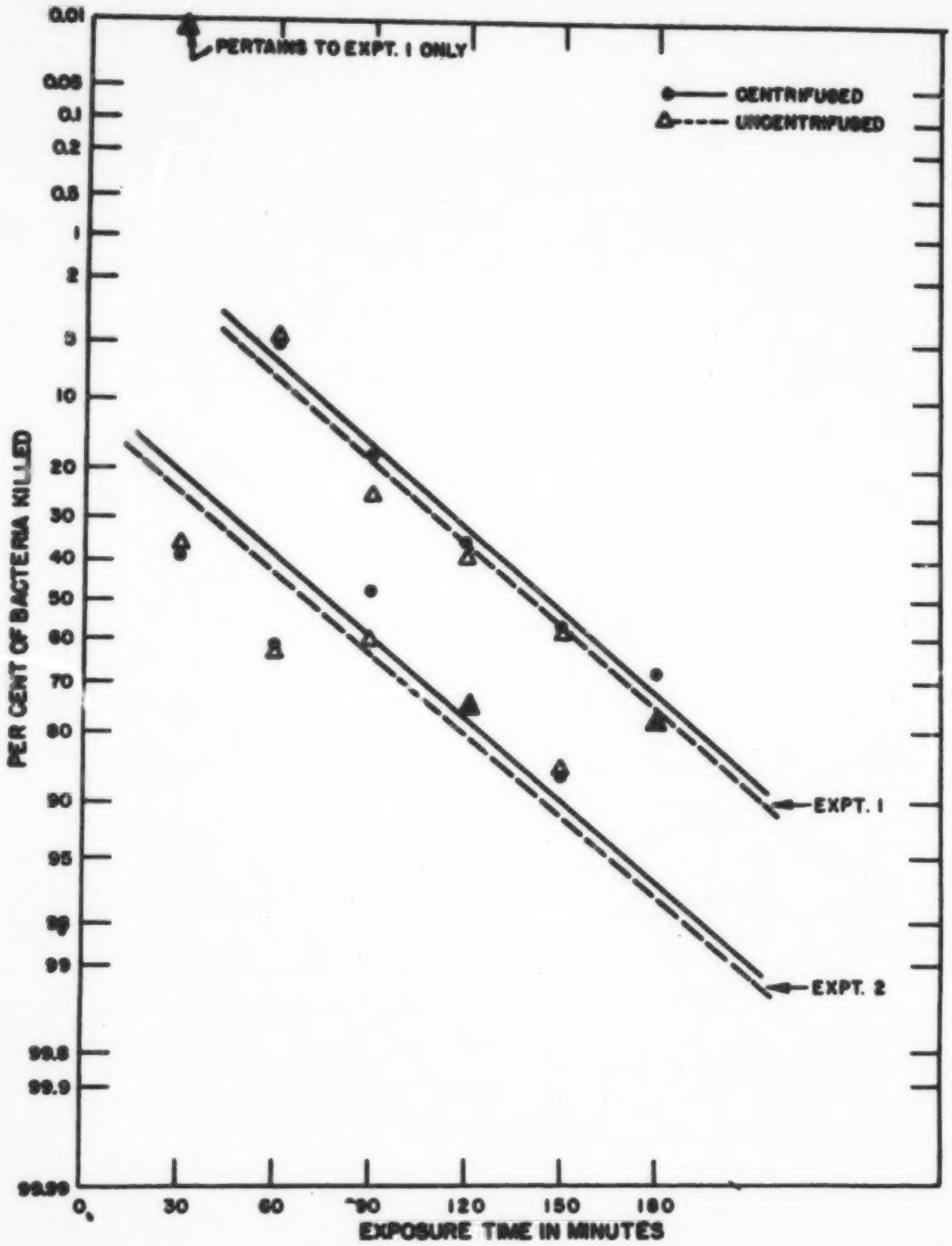
TABLE 5. COMPARISON OF SILVER NITRATE WITH SILVER FROM A FILTER DEVICE 40 ppb Ag[1] IN DISTILLED WATER AT pH 6.1

Average[2] percent of bacteria surviving for time indicated											
30 Min.		60 Min.		90 Min.		120 Min.		150 Min.		180 Min.	
$AgNO_3$	F[3]	$AgNO_3$	F	$AgNO_3$	F	$AgNO_3$	F	$AgNO_3$	F	$AgNO_3$	F
94.4	93.1	78.9	77.7	63.3	63.5	52.4	47.3	36.0	30.3	12.7	18.4

(1) By the rhodanine test at start of experiment.
(2) Average of 3 experiments (3 replicate flasks per experiment with each type of silver)
(3) F is silver from filter device.

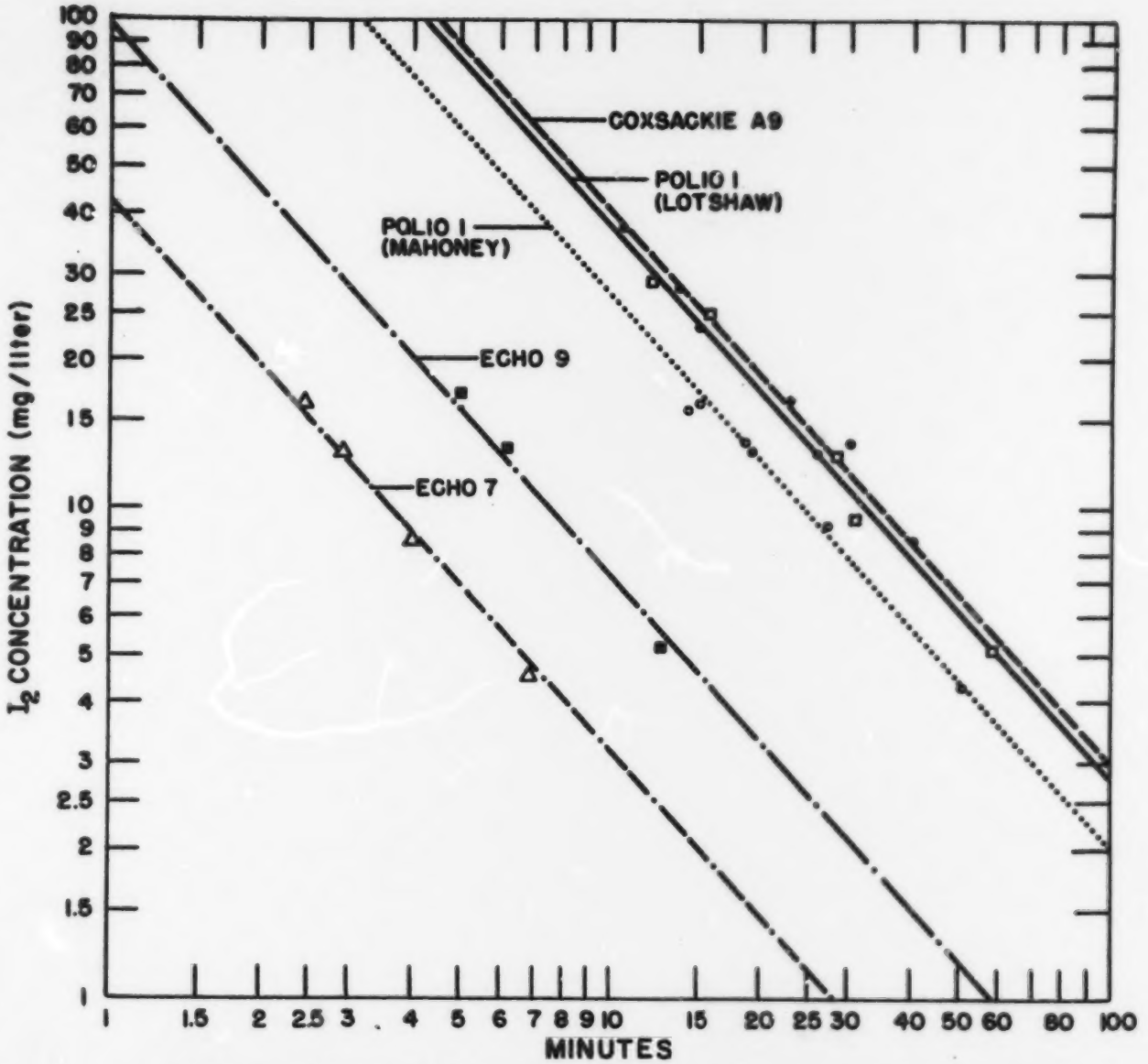
TABLE 6. EFFECT OF STORAGE AND TEMPERATURE ON IODINE RELEASING TABLETS

Storage time (hours)	Temperature (° F)	Number of tablets tested	% of original iodine remaining
18	120	2	68.0
72	120	2	30.5
168	120	2	5.4



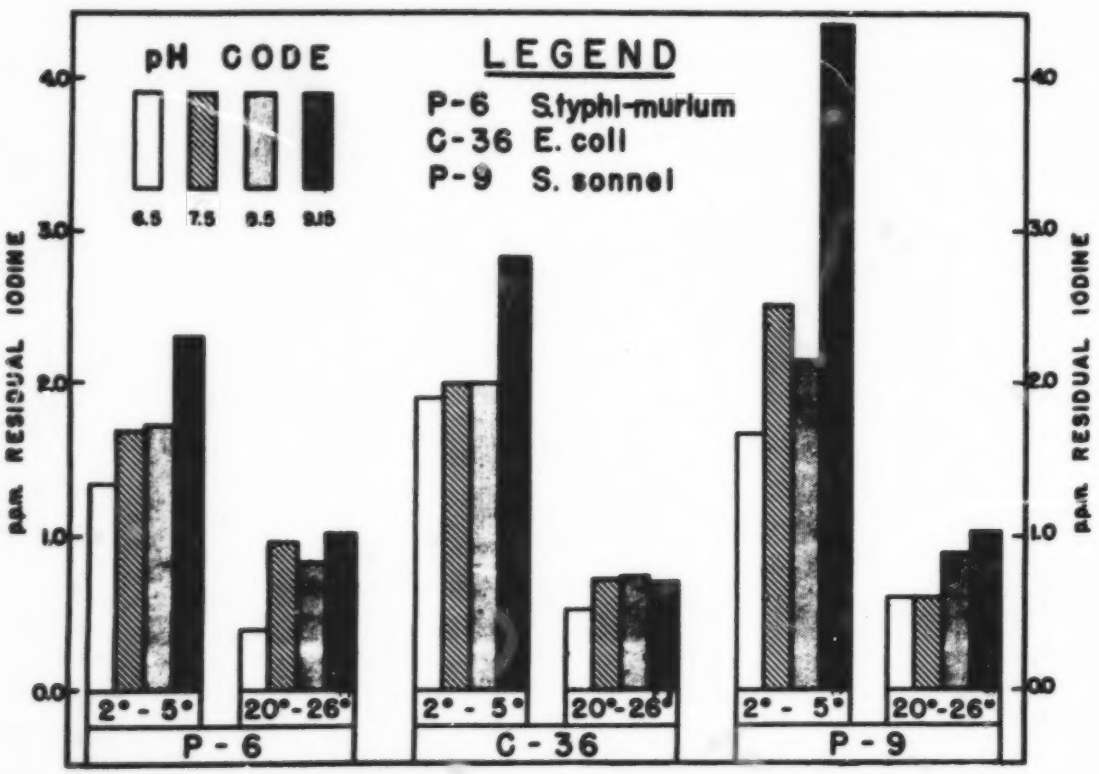
EFFECT OF CENTRIFUGING ON A COLLOIDAL SILVER PREPARATION (EQUAL VOLUMES OF CENTRIFUGED AND UNCENTRIFUGED MATERIAL USED IN ALL TESTS)

FIGURE 1



CONCENTRATION-TIME RELATIONSHIP FOR 99% DESTRUCTION OF ENTEROVIRUSES BY I_2 AT 15°C

FIGURE 2



AVERAGE ppm IODINE REQUIRED TO KILL ALL TEST BACTERIA IN 1 MINUTE

FIGURE 3